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Adsorption of metal ions by pecan shell-based granular activated carbons

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Abstract

The present investigation was undertaken to evaluate the adsorption effectiveness of pecan shell-based granular activated carbons (GACs) in removing metal ions (Cu^{2+}, Pb^{2+}, Zn^{2+}) commonly found in municipal and industrial wastewater. Pecan shells were activated by phosphoric acid, steam or carbon dioxide activation methods. Metal ion adsorption of shell-based GACs was compared to the metal ion adsorption of a commercial carbon, namely, Calgon's Filtrasorb 200. Adsorption experiments were conducted using solutions containing all three metal ions in order to investigate the competitive effects of the metal ions as would occur in contaminated wastewater. The results obtained from this study showed that acid-activated pecan shell carbon adsorbed more lead ion and zinc ion than any of the other carbons, especially at carbon doses of 0.2–1.0%. However, steam-activated pecan shell carbon adsorbed more copper ion than the other carbons, particularly using carbon doses above 0.2%. In general, Filtrasorb 200 and carbon dioxide-activated pecan shell carbons were poor metal ion adsorbents. The results indicate that acid- and steam-activated pecan shell-based GACs are effective metal ion adsorbents and can potentially replace typical coal-based GACs in treatment of metal contaminated wastewater.

Keywords: Granular activated carbon; Pecan shells; Freundlich model; Copper; Lead; Zinc

1. Introduction

Various carbonaceous materials, such as coal, lignite, coconut shells, wood and peat, are used in the production of commercial activated carbons. However, abundance and availability of agricultural byproducts make them good sources of raw materials for activated carbons. Harvesting and processing of various agricultural crops result in considerable quantities of agricultural byproducts. For example, the United States produced 315 million lbs of pecans in crop year 2001 (Agricultural Statistics, 2002) that resulted in approximately 158 million lbs of pecan shells. Additionally, pecans are of economic importance to many southern states, including Louisiana. Pecan shells have little or no economic value, and their disposal not only is costly but may also cause environmental problems. Conversion of pecan shells into activated carbons which can be used as adsorbents in water purification or the treatment of industrial and municipal effluents would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbons.

There are a number of published observations that show the utility of using pecan shells as activated carbons for the removal of metal ions and organic compounds (Toles et al., 1997, 1998, 1999; Johns et al., 1998, 1999; Wartelle and Marshall, 2001; Dastgheib and Rockstraw, 2001, 2002a,b). These studies utilized activated carbons that were produced by acid, steam or carbon dioxide activation. These studies showed that acid activation of pecan shells resulted in higher metal ion adsorption than activation by carbon dioxide or steam. This was particularly true when all three activation methods were compared in one publication (Johns et al., 1999). The investigations noted above generally

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observed metal ion binding only in the presence of a single metal ion, usually copper ion (Cu^{2+}). However, Dastgheib and Rockstraw (2002b) observed metal ion binding to pecan shell carbon in the presence of binary mixtures of various metals. Very little published literature report the competitive binding of a single metal ion in a mixture of metal ions in the presence of byproduct-based activated carbons, although this would be important to ascertain because metal ions do not usually exist in isolation in contaminated waters or wastewaters.

The present investigation was undertaken to evaluate the performance of pecan shell-based granular activated carbons (GACs) in the presence of solutions containing three common metals, namely, copper, lead and zinc ions. Pecan shells were activated by three different methods that included acid, steam or carbon dioxide. Metal ion adsorption of the pecan shell carbons was compared to a commercial, coal-based carbon and the results evaluated by means of the Freundlich adsorption model.

2. Methods

2.1. Materials

Pecan shell-based GACs produced by acid, steam or carbon dioxide activation were developed at the USDA-ARS, Southern Regional Research Center, New Orleans, LA, and were furnished for analysis. Upon receipt of the carbons, they were treated with 0.1 N HCl to remove ash, washed in distilled water to remove acid and dried at 110 °C before use. The commercial carbon, Filtrasorb 200, was procured from Calgon Carbon Corporation (Pittsburgh, PA) and used as is. Filtrasorb 200 is a coal-based GAC and is typical of coal-based carbons in metal ion adsorption properties. Cupric sulfate ($Cu_2SO_4 \cdot 5H_2O$) was purchased from Fisher Scientific (Pittsburgh, PA). Zinc chloride ($ZnCl_2$), lead nitrate [$Pb(NO_3)_2$] and nitric acid were obtained from Sigma-Aldrich Corp. (St. Louis, MO).

2.2. Preparation of metal ion solution

A standard solution consisting of 0.5 mM of each of the metal ions in acetate buffer (0.07 M sodium acetate and 0.03 M acetic acid) was prepared. The initial pH of the solution was 4.8.

2.3. Adsorption study

The carbon dosages used in this study were 0.05, 0.1, 0.2, 0.3, 0.5, 0.75, and 1.0 g per 100 ml of metal ion solution. The activated carbon slurry was stirred at 500 rpm on a magnetic stirrer for 24 h in order to achieve an equilibrium adsorption state. At the end of 24 h, the samples were removed from the stirrer and pH of the solution was measured. Initial and final pH values were generally within ±0.2 pH units of each other. Thereafter, an aliquot of the solution was drawn into a disposable syringe and filtered through a PTFE 0.45 μm filter in order to remove any carbon particles. The filtrate was stored at 4 °C and subsequently analyzed for metal ions using an Optima 3000 inductively coupled plasma (ICP) spectrometer (Perkin Elmer, Norwalk, CT).

3. Results and discussion

3.1. Metal ion adsorption by activated carbons

In Figs. 1–3 respectively, are presented, the percentage removal of Cu^{2+}, Pb^{2+}, and Zn^{2+} ions by pecan shell-based and commercial carbons. The data indicate that at carbon dosages at 0.2% and above, the acid-activated pecan shell carbon (PSA) removed more lead and zinc ions than any of the other carbons (Figs. 2

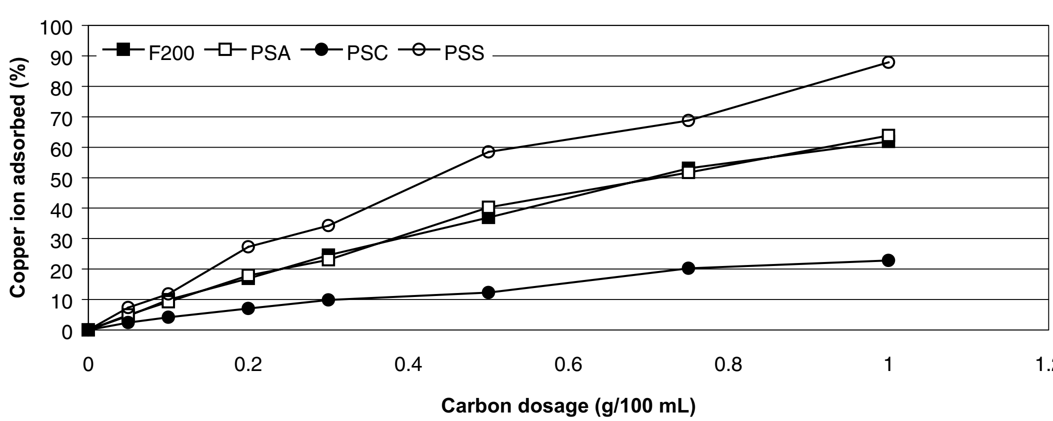

Fig. 1. Percentage of copper ion removed from solution by granular activated carbons. Abbreviations: F200 = Calgon Filtrasorb 200; PSA = phosphoric acid-activated pecan shell carbon; PSC = carbon dioxide-activated pecan shell carbon; PSS = steam-activated pecan shell carbon.

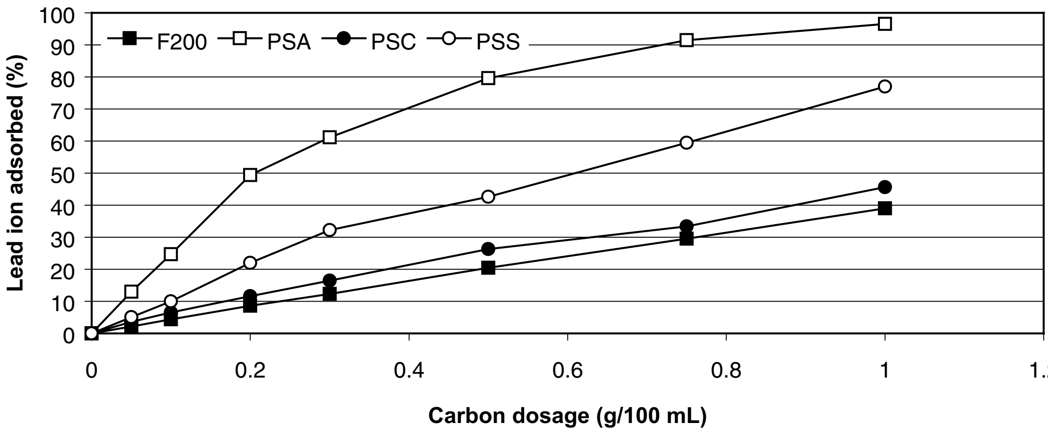

Fig. 2. Percentage of lead ion removed from solution by granular activated carbons. Abbreviations: F200 = Calgon Filtrasorb 200; PSA = phosphoric acid-activated pecan shell carbon; PSC = carbon dioxide-activated pecan shell carbon; PSS = steam-activated pecan shell carbon.

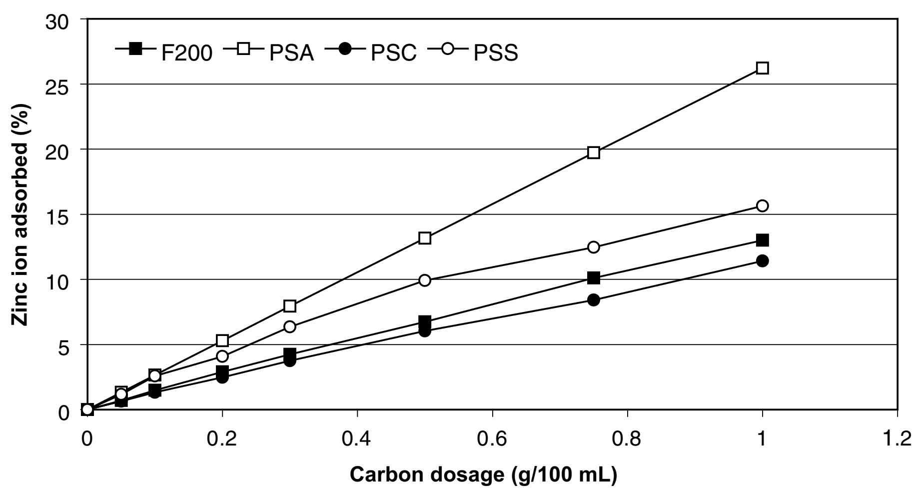

Fig. 3. Percentage of zinc ion removed from solution by granular activated carbons. Abbreviations: F200 = Calgon Filtrasorb 200; PSA = phosphoric acid-activated pecan shell carbon; PSC = carbon dioxide-activated pecan shell carbon; PSS = steam-activated pecan shell carbon.

and 3). Moreover, PSA removed more lead ion than the other carbons at dosage levels below 0.05% (Fig. 2). Steam-activated pecan shell carbon (PSS) adsorbed more copper ion than the other carbons (Fig. 1). In general, carbon dioxide activated pecan shell (PSC) and Filtrasorb 200 removed the least amount of the individual metal ions at the carbon dosages used in this study.

Since the adsorption studies included all three metal ions in the same solution at the same molar concentration, the amount of a particular metal ion adsorbed by the carbon indicated its ability to compete with the other metal ions in solution for the adsorption sites on the carbon. Carbon adsorption sites on PSS, PSA and PSC appeared to favor lead ions, followed by copper ions and zinc ions at the highest carbon dosage studied, namely, 1.0%. Only Filtrasorb 200 adsorbed more copper ion than lead ion, followed by zinc ion at the 1.0% dosage level. Therefore, adsorption preference for all the pecan shell-based carbons was $Pb^{2+} > Cu^{2+} > Zn^{2+}$, which agrees with predictions based on the ionic radius of the metals (e.g. Irving-Williams series) or cation electronegativity. The adsorption pattern of $Cu^{2+} > Pb^{2+} > Zn^{2+}$ for the commercial carbon may be due to different types of adsorption sites (hydrophobic or non-ionic versus ionic) that depend less on cation electronegativity on this carbon compared to the pecan shell carbons.

Greater adsorption of metal ions using phosphoric acid-activated pecan shell carbon compared to steam- or carbon dioxide-activated pecan shell carbons or even commercial carbons are consistent with observations found in the literature. However, the greater adsorption of copper ion by PSS found in this study is inconsistent with the results of Johns et al. (1999), who found greater copper ion adsorption with phosphoric acid-activated pecan shell carbon than with carbons made by either steam activation or carbon dioxide activation.

The observations of Johns et al. (1999) were made using a solution of copper ion and contained no other divalent metal ions. The presence of lead and zinc ions used in this study, in addition to copper ion, may have suppressed the adsorption of copper ion by PSA, perhaps more so than the presences of these ions suppressed the adsorption of copper ions by PSS.

3.2. Freundlich isotherms

The adsorption data in Figs. 1–3 were fitted to the Freundlich adsorption model. The basic Freundlich equation is:

$$x/m = kc^{1/n}$$

where, in our specific case, $x =$ amount of metal ion adsorbed, $m =$ mass or weight of carbon used, $x/m =$ concentration of metal ion adsorbed per mass or weight of carbon, $c =$ equilibrium concentration of the metal ion in solution, and k and n are empirical constants. A linear form of the Freundlich equation is represented by:

$$\log(x/m) = \log k + 1/n \log c$$

The linear form of the Freundlich equation was used to determine the empirical constants k and $1/n$. Values for these constants are given in Table 1.

Ng et al. (2002) found that for binding of geosmin to activated carbons, some of which were made from pecan shells, relatively higher k values represented overall greater binding of geosmin to the activated carbon at a series of carbon dosages. In this study, PSS had the highest k value for Cu^{2+} adsorption (Table 1). PSS also showed the greatest binding of copper ion over the range of carbon dosages used (Fig. 1). Moreover, for lead ion and zinc ion adsorption, PSA displayed the highest values for k compared to the other carbons (Table 1). Consequently, PSA showed the greatest adsorption of lead ion and copper ion (Figs. 2 and 3). Moreover, PSC and Filtrasorb 200 had the lowest k values and also the lowest adsorption of the four carbons. Empirically, k values may be used to predict differences in the abilities of different adsorbents to adsorb a particular adsorbate.

Table 1
Freundlich constants for metal ion adsorption[a]

Metal ion	Carbon type	$1/n$	k	r
Cu^{2+}	F200	0.447	6.10	0.92
	PSA	0.413	6.84	0.88
	PSC	2.76	0.001	0.78
	PSS	**0.226**	**18.1**	**0.75**
Pb^{2+}	F200	0.241	14.6	0.89
	PSA	**0.322**	**64.2**	**0.98**
	PSC	0.770	1.94	0.825
	PSS	0.247	34.7	0.72
Zn^{2+}	F200	0.804	0.287	0.98
	PSA	**0.039**	**13.9**	**0.93**
	PSC	1.30	6.62	0.82
	PSS	2.80	7.38	0.87

[a] Freundlich constants $1/n$ and k were obtained from the linear form of the Freundlich equation using data from Figs. 1–3. The values for r are the correlation coefficients for the linear relationships. Abbreviations are: F200 = Calgon Filtrasorb 200; PSA = phosphoric acid-activated pecan shell; PSC = carbon dioxide-activated pecan shell; PSS = steam-activated pecan shell. Values in *boldface* represent carbons where the highest adsorption for a particular metal occurred.

4. Conclusions

The results indicate that phosphoric acid-activated and steam-activated pecan shell carbons remove the metal ions copper, lead and zinc from solution better than the commercial carbon, Calgon's Filtrasorb 200, at carbon dosages between 0.05% and 1.0%. Although 100% metal ion adsorption was not attained at these carbon dosages, the results give a good picture of the utility of PSA and PSS as metal ion adsorbents. In the dosage range employed, PSA and PSS would be better choices for removal of metal ions than a commercial coal-based carbon.

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